Rec'd PCT/PTO 20 MAR 2002

FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: **220713US0PCT**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR: 10/088075

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/09072	**15 September 2000**	**20 September 1999**

TITLE OF INVENTION
ELECTROLYTIC TRANSFORMATION OF FURAN OR FURAN DERIVATIVES

APPLICANT(S) FOR DO/EO/US
Hermann PUETTER

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include itens (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☒ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Notice of Priority/ Form PTO-1449
PCT/IB/304/Amended Sheets 11 and 12

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/088075	PCT/EP00/09072	220713US0PCT

24. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

	CALCULATIONS	PTO USE ONLY
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**		
☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**		
☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**		
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**		
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	**$890.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$0.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	20 - 20 =	0	x $18.00	**$0.00**	
Independent claims	1 - 3 =	0	x $84.00	**$0.00**	
Multiple Dependent Claims **(check if applicable).**			☐	**$0.00**	
TOTAL OF ABOVE CALCULATIONS =				**$890.00**	
☐ Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				**$0.00**	
SUBTOTAL =				**$890.00**	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +				**$0.00**	
TOTAL NATIONAL FEE =				**$890.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐				**$0.00**	
TOTAL FEES ENCLOSED =				**$890.00**	
				Amount to be: refunded	$
				charged	$

a. ☒ A check in the amount of **$890.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. ________ in the amount of ________ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

22850

Surinder Sachar
Registration No. 34,423

Surinder Sachar

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

March 20 2002

DATE

10/088075
JC13 Rec'd PCT/PTO 20 MAR 2002

220713US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF	:
HERMANN PUETTER	: ATTN: APPLICATION DIVISION
SERIAL NO: NEW U.S. PCT APPLN (Based on PCT/EP00/09072)	:
FILED: HEREWITH	:
FOR: ELECTROLYTIC TRANSFORMATION OF FURAN OR FURAN DERIVATIVES	

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows:

IN THE CLAIMS

Please amend the claims as shown in the marked-up copy following this amendment to read as follows:

3. (Amended) A process as claimed in claim 1, wherein at least one electrode is in contact with at least one hydrogenation catalyst, in particular with a noble metal.

7. (Amended) A process as claimed in claim 1, wherein at least one of the electrodes used is a gas diffusion electrode.

8. (Amended) A process as claimed in claim 1, wherein at least one of the electrodes used is a composite comprising at least one conventional electrode material and at least one material for a gas diffusion electrode.

10. (Amended) A process as claimed in claim 3, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

11. (Amended) A process as claimed in claim 1, wherein the alkoxylated furan compound (B) produced in step (i) is reacted in step (ii) to form at least one ring-opened butane derivative.

Please add the following new claims:

13. (New) A process as claimed in claim 2, wherein at least one electrode is in contact with at least one hydrogenation catalyst, in particular with a noble metal.

14. (New) A process as claimed in claim 4, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

15. (New) A process as claimed in claim 5, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

16. (New) A process as claimed in claim 6, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

17. (New) A process as claimed in claim 7, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

18. (New) A process as claimed in claim 8, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

19. (New) A process as claimed in claim 9, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

20. (New) A process as claimed in claim 13, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

REMARKS

Claims 1-20 are active in the present application. Claims 3, 7-8 and 10-11 have been amended to remove multiple dependencies. Claims 13-20 are new claims. Support for the new claims is found in the original claims. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.

Norman F. Oblon
Attorney of Record
Registration No. 24,618

Stefan U. Koschmieder, Ph.D.
Registration No. 50,238

22850

(703) 413-3000
Fax #: (703)413-2220
NFO/kst

I:\atty\SUKOS\220713us-pr.wpd

Marked-Up Copy
Serial No:

Amendment Filed on:
3-20-2002

IN THE CLAIMS

--3. (Amended) A process as claimed in claim 1 [or 2], wherein at least one electrode is in contact with at least one hydrogenation catalyst, in particular with a noble metal.

7. (Amended) A process as claimed in [any of claims 1 to 6] claim 1, wherein at least one of the electrodes used is a gas diffusion electrode.

8. (Amended) A process as claimed in [any of claims 1 to 6] claim 1, wherein at least one of the electrodes used is a composite comprising at least one conventional electrode material and at least one material for a gas diffusion electrode.

10. (Amended) A process as claimed in [any of claims 3 to 9] claim 3, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

11. (Amended) A process as claimed in [any of claims 1 to 10] claim 1, wherein the alkoxylated furan compound (B) produced in step (i) is reacted in step (ii) to form at least one ring-opened butane derivative.

Claims 13-20 (New).--

THE FOLLOWING IS THE ENGLISH TRANSLATION OF THE ARTICLE 34 AMENDED SHEETS (pages 11 and 12)

<u>**as enclosed to IPER/JP**</u>

We claim:

1. A process for the electrolytic transformation of at least one furan-based starting compound (A) in an electrolysis circuit which comprises both the steps (i) and (ii):
   (i) electrolytic oxidation of furan or a substituted furan or a mixture of two or more thereof to give
   (a) at least one alkoxylated furan compound (B) which has a C-C double bond in the five-membered heterocyclic ring, and
   (b) hydrogen;
   (ii) hydrogenation of this C-C double bond using the hydrogen obtained in parallel at the cathode in step (i) or hydrogen fed to the electrolysis circuit from outside or by electrocatalytic hydrogenation,

   wherein the process is carried out in an electrolysis cell in which at least one hydrogenation catalyst is present.

2. A process as claimed in claim 1, which proceeds in an undivided electrolysis cell.

3. A process as claimed in claim 1 or 2, wherein at least one electrode is in contact with at least one hydrogenation catalyst, in particular with a noble metal

4. A process as claimed in claim 3, wherein the hydrogenation catalyst, in particular the noble metal, has been applied to a graphite felt.

5. A process as claimed in claim 3, wherein the hydrogenation catalyst has been washed onto the at least one electrode.

6. A process as claimed in claim 3, wherein the hydrogenation catalyst is brought in the form of a suspension into contact with the at least one electrode.

7. A process as claimed in any of claims 1 to 6, wherein at least one of the electrodes used is a gas diffusion electrode.

8. A process as claimed in any of claims 1 to 6, wherein at least one of the electrodes used is a composite comprising at least one conventional electrode material and at least one material for a gas diffusion electrode.

9. A process as claimed in claim 8, wherein the conventional electrode material comprises carbon.

10. A process as claimed in any of claims 3 to 9, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

11. A process as claimed in any of claims 1 to 10, wherein the alkoxylated furan compound (B) produced in step (i) is reacted in step (ii) to form at least one ring-opened butane derivative.

12. A process as claimed in claim 11, wherein the ring-opened butane derivative is 1,1,4,4-tetramethoxybutane or a substituted 1,1,4,4-tetramethoxybutane.

Abstract

A process for the electrolytic transformation of at least one furan derivative (A) in an electrolysis circuit comprises both the steps (i) and (ii):

(i) electrolytic oxidation of furan or a substituted furan or a mixture of two or more thereof to give

(a) at least one furan derivative (B) which has a C-C double bond in the five-membered heterocyclic ring, and

(b) hydrogen;

(ii) hydrogenation of this C-C double bond using the hydrogen obtained in parallel at the cathode in step (i) or hydrogen fed to the electrolysis circuit from outside or electrocatalytic hydrogenation,

wherein the process is carried out in an electrolysis cell in which at least one hydrogenation catalyst is present.

10/088075
JC13 Rec'd PCT/PTO 20 MAR 2002

O.Z.0050/50737

as originally filed

Electrolytic transformation of furan or furan derivatives

The present invention relates to a process for the electrolytic transformation of furan or one or more furan derivatives.

An objective of preparative organic electrochemistry is to utilize the processes occurring at the two electrodes in an electrochemical process in parallel. Processes in which the two electrode processes which occur in an undivided cell can be utilized for the reaction of chemical compounds are of particular interest.

An example of such a process is the oxidative dimerization of 2,6-dimethylphenol, which is coupled with the dimerization of maleic esters (M.M. Baizer, in: H. Lund, M.M. Baizer (Eds), Organic Electrochemistry, Marcel Dekker, New York, 1991, pages 1442 ff.).

A further example is the coupled synthesis of phthalide and t-butylbenzaldehyde (DE 196 18 854).

However, it is also possible to utilize the cathode process and the anode process to produce a single product or to decompose a starting material. Examples of such electrochemical processes are the production of butyric acid (Y. Chen, T. Chou, J. Chin. Inst. Chem. Eng. 27 (1996) pages 337-345), the anodic dissolution of iron, which is coupled with the cathodic formation of ferrocene (T. Iwasaki et al., J. Org. Chem. 47 (1982) pages 3799 ff.) or the decomposition of phenol (A. P. Tomilov et al., Elektrokhimiya 10 (1982) page 239).

An example of a process in which a furan derivative is reacted in an undivided electrolysis cell and the two electrode processes are utilized is the oxidation of furancarboxylic acid with subsequent ring opening to form 1-carboxymethyl-4,4-dimethoxypropene which is hydrogenated in a further step to give the saturated propane derivative (T. Iwasaki et al., J. Org. Chem. 47 (1982) pages 3799 ff.). However, this is not a catalytic hydrogenation, but a direct electroreduction. In this case, however, it is not the furan which is reacted but the α,β-unsaturated ester, i.e. a class of substances whose electrochemical reduction is known. Furthermore, the

ring opening and the subsequent hydrogenation do not occur directly on the anodically generated product but on a fragment which has undergone further oxidation and has one less carbon atom.

An electrochemical oxidation of furan or a furan derivative with retention of the heterocyclic ring structure and subsequent hydrogenation involving hydrogenation of a double bond which is present in the ring structure after oxidation is, however, not known in processes in which both electrode processes are utilized.

It is an object of the present invention to provide an electrochemical process which preferably proceeds in an undivided electrolysis cell and in which furan or a substituted furan is oxidized in one electrode process with retention of the heterocyclic ring structure and this oxidation product is hydrogenated by means of hydrogen which is formed as product in the other electrode process or is transferred as hydrogen equivalent to the furan derivative in the sense of an electrocatalysis.

We have found that this object is achieved by a process for the electrolytic transformation of at least one furan derivative (A) in an electrolysis circuit which comprises both the steps (i) and (ii):

(i) electrolytic oxidation of furan or a substituted furan or a mixture of two or more thereof to give

(a) at least one furan derivative (B) which has a C-C double bond in the five-membered heterocyclic ring, and

(b) hydrogen;

(ii) hydrogenation of this C-C double bond using the hydrogen obtained in parallel at the cathode in step (i) or hydrogen fed to the electrolysis circuit from outside or electrocatalytic hydrogenation,

wherein the process is carried out in an electrolysis cell in which at least one hydrogenation catalyst is present.

The process preferably occurs in an undivided electrolysis cell.

Apart from furan, the following compounds may be mentioned as examples of preferred substituted furans:

furfural(furan-2-aldehyde), alkyl-substituted furans, furans substituted by -CHO, -COOH, -COOR, where R is an alkyl, benzyl or aryl group, in particular a C_1-C_4-alkyl group, -CH(OR_1)(OR_2), where R_1 and R_2 may be identical or different and are each an alkyl, benzyl or aryl group, in particular a C_1-C_4-alkyl group, and -CN groups in the 2, 3, 4 or 5 position.

In the reaction according to the present invention of organic compounds, it is possible to use solvents and electrolyte salts as are described in H. Lund, M. M. Baizer, (Eds) "Organic Electrochemistry", 3rd Edition, Marcel Dekker, New York 1991.

The oxidation is, according to the present invention, preferably carried out in the presence of methanol or in the presence of ethanol or a mixture thereof, but preferably in the presence of methanol. The substrates can simultaneously act as reactant and solvent.

Solvents which can be used in the reaction include not only furan and substituted furan and the compound used for the oxidation but also all suitable alcohols in general.

Electrolyte salts which can be used in the process of the present invention include NaBr and also, for example, alkali metal and/or alkaline earth metal halides, with bromides, chlorides and iodides being possible as halides. Ammonium halides can likewise be used.

Pressures and temperatures can assume values as are customarily employed in catalytic hydrogenations.

In a preferred embodiment of the process of the present invention, the reaction temperature T is $< 50°C$, preferably $< 25°C$, the pressure p is < 3 bar and the pH is in the neutral region.

In a preferred embodiment of the process of the present invention, intermediates are fed in in addition to the starting materials which are introduced into the undivided electrolysis cell. The term intermediate refers to a product which is obtained as furan derivative (B) in step (i) of the above-described process by

electrolytic oxidation of furan or a substituted furan or a mixture of two or more thereof and is therefore present in the electrolysis circuit. The concentration of the additional intermediates is set by means of customary electrochemical and electrocatalytic parameters, for example current density, type of catalyst and amount of catalyst, or the intermediate is added to the circuit.

As regards the specific choice of the electrode material, there is no restriction in the process of the present invention as long as the electrodes are suitable for the above-described process.

Preference is given to using graphite anodes in the undivided cell.

As far as the geometry of the electrodes in the undivided electrolysis cell is concerned, there are essentially no restrictions in the process of the present invention. Preferred geometries are, for example, flat parallel electrode arrangements and annular or cylindrical electrode arrangements.

In a preferred embodiment of the invention, at least one electrode is in contact with at least one hydrogenation catalyst. In a particularly preferred embodiment, the at least one hydrogenation catalyst is part of a gas diffusion electrode. In a further preferred embodiment of the invention, at least one electrode is a graphite electrode which is coated with noble metal and is in the form of a plate, mesh or felt. In another preferred embodiment of the invention, the hydrogenation catalyst in the form of a suspension in the electrolyte is continually brought into contact with at least one electrode. Here, the hydrogenation catalyst, i.e. the catalytically active material, is pumped around in the cell or washed onto an appropriately structured cathode or anode. Such a wash-coated electrode is described, for example, in DE 196 20 861.

If a gas diffusion electrode is used for at least one of the electrodes, the material from which the gas diffusion electrode is made can in principle have been processed so that the gas diffusion electrode can be used as electrode without support material. In a preferred embodiment, an alternative is provided by at least one of the electrodes used being a composite which comprises at least one conventional electrode material and at least one material for a gas diffusion electrode.

It is conceivable for this further electrode material to comprise one electric conductor or a plurality of electric conductors.

It is in principle conceivable for the composite comprising the conventional electrode material and the material of the gas diffusion electrode to be used as one electrode in the process of the present invention together with one or more suitable counterelectrodes.

These one or more suitable counterelectrodes are subject to no restrictions in respect of their geometry and their chemical composition, as long as the process of the present invention can be carried out using them.

In a preferred embodiment of the process of the present invention, the further electrode material which forms a composite with the gas diffusion electrode material is also used as counterelectrode to the gas diffusion electrode. This is achieved by a bipolar electrode arrangement.

In a preferred embodiment of the process of the present invention, graphite and/or carbon fiber paper are/is used as base material for the gas diffusion electrode. The catalyst composition is applied thereto.

As support material on which the gas diffusion electrode material is supported, preference is given, in the process of the present invention, to further electrode materials comprising carbon.

In the process of the present invention, a C-C double bond is, as described above, hydrogenated electrocatalytically using the hydrogen obtained in step (i) or using the corresponding hydrogen equivalents in the sense of an electrolysis. In this hydrogenation, the compound to be hydrogenated is preferably brought into contact with one or more hydrogenation catalysts.

As regards the choice of hydrogenation-active catalysts, there are in principle no restrictions for the purposes of the process of the present invention. All catalysts known from the prior art can be used. Mention may be made, inter alia, of the

metals of transition groups I, II and VIII of the Periodic Table, in particular Co, Ni, Fe, Ru, Rh, Re, Pd, Pt, Os, Ir, Ag, Cu, Zn and Cd.

For example, it is possible to use the metals in finely divided form. Examples are Raney Ni, Raney Co, Raney Ag and Raney Fe, each of which may further comprise other elements such as Mo, Cr, Au, Mn, Hg, Sn or S, Se, Te, Ge, Ga, P, Pb, As, Bi or Sb.

It is naturally also possible for the hydrogenation-active materials described to comprise a mixture of two or more of the hydrogenation metals mentioned, which may, if desired, be combined with, for example, one or more of the abovementioned elements.

Of course, it is also conceivable for the hydrogenation-active material to be applied to an inert support. As such support systems, it is possible to use, for example, activated carbon, graphite, carbon black, silicon carbide, aluminum oxide, silicon dioxide, titanium dioxide, zirconium dioxide, magnesium oxide, zinc oxide or mixtures of two or more thereof, e.g. as a suspension or as finely divided granulated material.

In a preferred embodiment of the present invention, the hydrogenation-active material is applied to the base material of the gas diffusion electrode.

Accordingly, the present invention also provides a process as described above in which the base material of the gas diffusion electrode is laden with a hydrogenation-active material.

As hydrogenation-active material with which the gas diffusion electrode system is laden, it is possible to use all hydrogenation catalysts as described above. Of course, it is also possible to use a mixture of two or more of these hydrogenation catalysts as hydrogenation-active material.

It is naturally also conceivable in the process of the present invention for the gas diffusion electrode material to be laden with hydrogenation-active material and for use to be made of additional hydrogenation-active material which is identical to or different from that with which the gas diffusion electrode material is laden.

The process of the present invention, as described above, in principle allows, in particular, a choice between using the electrocatalytically active electrode, i.e. the electrode which is in contact with a hydrogenation catalyst, as cathode or as anode or as cathode and anode.

The present invention therefore also provides a process as described above in which the electrocatalytically active electrode, for example a gas diffusion electrode, is used as cathode and/or as anode.

Furthermore, the present invention provides a process as described above in which the furan derivative (B) produced is reacted to form at least one ring-opened butane derivative. The ring-opened butane derivative is preferably 1,1,4,4-tetramethoxybutane or a substituted 1,1,4,4-tetramethoxybutane.

The following examples illustrate the present invention.

Examples

Example 1

An undivided cell having 6 annular electrodes with a surface area per side of 15.7 cm^2 was used. The electrodes were separated from one another by means of 5 spacer meshes having a thickness of 0.7 mm.

The uppermost and lowermost electrodes were connected to electric power. The uppermost electrode was connected as an anode, the lowermost electrode was connected as a cathode and the electrodes between them were bipolar.

The electrodes comprised graphite disks which had a thickness of 5 mm each and were coated on one side with gas diffusion electrode material. This material was in turn coated with 10 g of platinum/m^2.

The gas diffusion electrode was connected as cathode.

The electrolysis batch consisted of 30 g of furan, 57.63 g of 2,5-dimethoxydihydrofuran, 2 g of NaBr and 112 g of methanol.

Electrolysis was carried out at 0.47 A and 15°C. During the reaction, the cell voltage rose from 13.0 V to 17.4 V. The electrolysis was monitored by gas chromatography.

After 1 F/mol of furan, the proportion of furan in GC-percent by area had dropped from 22.9% to 18.8%, while the proportion of dimethoxydihydrofuran had increased from 32.2% to 34.5%. At the same time, 1.4% of 2,5-dimethoxytetrahydrofuran were formed.

Example 2

The cell arrangement corresponded to that of Example 1. Instead of a Pt-laden gas diffusion cathode, use was made of a gas diffusion electrode laden with 5.2 g/m^2 of Pd.

The electrolysis batch consisted of 60 g of furan, 126.2 g of 2,5-dimethoxydihydrofuran, 2 g of NaBr and 234.4 g of methanol.

Electrolysis was carried out at 0.47 A and about 18°C. The cell voltage rose from 19.1 V to 26.4 V. The electrolysis was monitored by gas chromatography.

After 1 F/mol of furan, the proportion of furan in GC-percent by area had dropped from 22.8% to 18.0%, while the proportion of dimethoxydihydrofuran had increased from 30.7% to 30.9%. At the same time, 0.7% of 2,5-dimethoxytetrahydrofuran were formed.

Example 3

The cell arrangement corresponded to that of Example 1. Instead of a gas diffusion cathode, use was made of a gas diffusion electrode laden with 5.2 g of Pd/m^2 as anode.

The electrolysis batch consisted of 30 g of furan, 57.4 g of 2,5-dimethoxydihydrofuran, 2 g of NaBr and 110.6 g of methanol.

Electrolysis was carried out at 0.48 A and about 17°C. The cell voltage rose from 16.3 V to 19.5 V. The electrolysis was monitored by gas chromatography.

After 1 F/mol of furan, the proportion of furan in GC-percent by area had dropped from 22.7% to 16.9%, while the proportion of 2,5-dimethoxydihydrofuran in GC-percent by area remained constant at 30%. At the same time, 3.3% of 2,5-dimethoxytetrahydrofuran were formed.

Example 4

A cell having 5 annular electrodes with a surface area of 44 cm^2 was used. The electrodes were each separated from one another by 2 spacer meshes having a thickness of 1 mm.

The electrodes comprised graphite disks which had a thickness of 5 mm each and had been coated on the sides in contact with electrolyte, both anodic and cathodic, with gas diffusion electrode material. This material was covered with 0.5 mg of Pd/cm^2.

The electrolysis batch consisted of 120 g of furan, 229.9 g of 2,5-dimethoxydihydrofuran, 8 g of NaBr and 542.5 g of MeOH.

The electrolysis was carried out at 1.32 A to a power usage of 2 F/mol of furan, and the electrolysis temperature was 17°C. The electrolysis was monitored by gas chromatography.

The furan concentration had decreased from 21.2% by area to 13.4% by area, and the 2,5-dimethoxydihydrofuran concentration had decreased from 25.2% by area to 23.3% by area.

At the same time, 3.5% by area of dimethoxytetrahydrofuran had been formed. Ring opening took place in this experiment.

1,1,4,4-tetramethoxy-cis-butene [1.3% by area] was formed from 2,5-dimethoxydihydrofuran and 4.2% by area of 1,1,4,4-tetramethoxybutane were formed from 2,5-dimethoxytetrahydrofuran.

This means that the amount of furan has decreased by one third, the stage of methoxylation (ring-closed and ring-opened) has remained virtually constant and

the further hydrogenation has taken place to a great extent which corresponds to the decrease in the amount of furan.

Example 5

Reaction of furan in the presence of a hydrogenation catalyst

The reaction took place in a frame cell having three anodes and three cathodes comprising a flexible graphite board "Sigrabond CFC 07G" from SGL, Meitingen, coated on one side with a graphite mesh. One anode and one cathode were made monopolar and served as end plates while the other two electrodes were connected so as to act as two bipolar electrodes. The electrodes were kept the intended distance apart by means of conventional spacer meshes. The spacing was 5 mm. The area of each electrode was 4.8 x 9.5 cm.

In this cell, an electrolyte consisting of 75 g of furan, 222 g of methanol, 3 g of NaBr and 0.5 g of activated carbon containing 10% of palladium was reacted at 26°C. At a current of 1.36 A and a mean cell voltage of 24 V, electrolysis was carried out for 7.5 hours with the catalyst-containing suspension continually being pumped around the cell circuit. At the end, the furan content had dropped to 55% of the initial value. With a selectivity of about 95%, 2,5-dimethoxydihydrofuran, 2,5-dimethoxytetrahydrofuran and 1,1,4,4-tetramethoxybutane had been formed in a ratio of 1:0.75:1.55. The proportion of simultaneously methoxylated and hydrogenated products was thus 70%.

We claim:

1. A process for the electrolytic transformation of at least one furan derivative (A) in an electrolysis circuit which comprises both the steps (i) and (ii):
   (i) electrolytic oxidation of furan or a substituted furan or a mixture of two or more thereof to give
   (a) at least one furan derivative (B) which has a C-C double bond in the five-membered heterocyclic ring, and
   (b) hydrogen;
   (ii) hydrogenation of this C-C double bond using the hydrogen obtained in parallel at the cathode in step (i) or hydrogen fed to the electrolysis circuit from outside or electrocatalytic hydrogenation,
   wherein the process is carried out in an electrolysis cell in which at least one hydrogenation catalyst is present.

2. A process as claimed in claim 1, which proceeds in an undivided electrolysis cell.

3. A process as claimed in claim 1 or 2, wherein at least one electrode is in contact with at least one hydrogenation catalyst, in particular with a noble metal.

4. A process as claimed in claim 3, wherein the hydrogenation catalyst, in particular the noble metal, has been applied to a graphite felt.

5. A process as claimed in claim 3, wherein the hydrogenation catalyst has been washed onto the at least one electrode.

6. A process as claimed in claim 3, wherein the hydrogenation catalyst is brought in the form of a suspension into contact with the at least one electrode.

7. A process as claimed in any of claims 1 to 6, wherein at least one of the electrodes used is a gas diffusion electrode.

8. A process as claimed in any of claims 1 to 6, wherein at least one of the electrodes used is a composite comprising at least one conventional electrode material and at least one material for a gas diffusion electrode.

9. A process as claimed in claim 8, wherein the conventional electrode material comprises carbon.

10. A process as claimed in any of claims 3 to 9, wherein the at least one electrode which is in contact with a hydrogenation catalyst is used as cathode or as anode or as cathode and anode.

11. A process as claimed in any of claims 1 to 10, wherein the furan derivative (B) is reacted to form at least one ring-opened butane derivative.

12. A process as claimed in claim 11, wherein the ring-opened butane derivative is 1,1,4,4-tetramethoxybutane or a substituted 1,1,4,4-tetramethoxybutane.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro

(43) Internationales Veröffentlichungsdatum
29. März 2001 (29.03.2001)

PCT

(10) Internationale Veröffentlichungsnummer
WO 01/21857 A1

(51) Internationale Patentklassifikation[7]: C25B 3/00, C07D 307/20

(21) Internationales Aktenzeichen: PCT/EP00/09072

(22) Internationales Anmeldedatum: 15. September 2000 (15.09.2000)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
199 44 989.9 20. September 1999 (20.09.1999) DE

(71) Anmelder *(für alle Bestimmungsstaaten mit Ausnahme von US)*: BASF AKTIENGESELLSCHAFT [DE/DE]; 67056 Ludwigshafen (DE).

(72) Erfinder; und
(75) Erfinder/Anmelder *(nur für US)*: PÜTTER, Hermann [DE/DE]; Haardter Strasse 1a, 67433 Neustadt (DE).

(74) Anwalt: ISENBRUCK, Günter; Bardehle, Pagenberg, Dost, Altenburg, Geissler, Isenbruck, Theodor-Heuss-Anlage 12, 68165 Mannheim (DE).

(81) Bestimmungsstaaten *(national)*: CA, JP, US.

(84) Bestimmungsstaaten *(regional)*: europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Veröffentlicht:
— *Mit internationalem Recherchenbericht.*
— *Vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen.*

(54) Title: METHOD FOR THE ELECTROLYTIC CONVERSION OF FURANE OR FURANE DERIVATIVES

(54) Bezeichnung: VERFAHREN ZUR ELEKTROLYTISCHEN UMWANDLUNG VON FURAN ODER FURANDERIVATEN

(57) Abstract: The invention relates to electrolytic conversion of at least one furane derivative (A) in an electrolytic circuit, comprising steps (i) and (ii): (i) electrolytic oxidation of furane or a substituted furane or a mixture of two or more of said furanes to obtain (a) at least one furane derivative (B) exhibiting a C-C double bond in a heterocyclic five-membered ring and (b) hydrogen, (ii) hydrogenation of said C-C double bond using hydrogen obtained from step (i) in a parallel process occurring at said cathode or external-source hydrogen added to said electrolytic circuit or electrocatalytic hydrogenation. The invention is characterized in that said method is performed in an electrolysis cell which has at least one hydrogenation catalyst.

(57) Zusammenfassung: Verfahren zur elektrolytischen Umwandlung mindestens eines Furanderivates (A) in einem Elektrolysekreis, das die beiden Schritte (i) und (ii) umfaßt: (i) Elektrolytische Oxidation von Furan oder eines substituierten Furans oder eines Gemisches aus zwei oder mehreren davon unter Erhalt (a) mindestens eines, im heterocyclischen Fünfring eine C-C-Doppelbindung aufweisenden Furanderivates (B), und (b) Wasserstoff, (ii) Hydrierung dieser C-C-Doppelbindung unter Verwendung des in Schritt (i) parallel an der Kathode erhaltenen Wasserstoffs oder von dem Elektrolysekreis von außen zugeführtem Wasserstoff oder elektrokatalitische Hydrierung, dadurch gekennzeichnet, daß das Verfahren in einer Elektrolysezelle durchgeführt wird, die mindestens einen Hydrierkatalysator umfaßt.

WO 01/21857 A1

Declaration, Power of Attorney

0050/050737

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Electrolytic transformation of furan or furan derivatives

the specification of which

[ ] is attached hereto.

[ ] was filed on ____________________ as

Application Serial No. ____________________

and amended on ____________________.

[x] was filed as PCT international application

Number PCT/EP00/09072

on September 15, 2000

and was amended under PCT Article 19

on ____________________ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above–identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)–(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed	
19944989.9	*Germany*	*20 September 1999*	[x] Yes	[ ] No

pdusopct001 - 55

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number) (Filing Date)

(Application Number) (Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	**Filing Date**	**Status (pending, patented, abandoned)**

And we (I) hereby appoint:

10

Norman F. Oblon, Registration Number 24, 618;
Marvin J. Spivak Registration Number 24, 913;
Gregory J. Maier, Registration Number 25, 599;
William E. Beaumont, Registration Number 30, 996;
Steven B. Kelber, Registration Number 30, 073;
Jean–Paul Lavalleye, Registration Number 31, 451;
Timothy R. Schwartz, Registration Number 32, 171;
Stephen G. Baxter, Registration Number 32, 884;
Richard L. Treanor, Registration Number ~~36, 379~~;
Robert W. Hahl, Registration Number 33, 893, our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact ~~all~~ business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

pdusopet001 - 55

~~*Hermann Pütter*~~
NAME OF INVENTOR

Hermann Pütter

Signature of Inventor

Date January 25, 2002

Haardter Str. 1a
67433 Neustadt
Germany
Citizen of: Germany
Post Office Address: same as residence